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## TECHNICAL TRANSLATION

THE CHARACTERISTICS OF HYDROGEN
AND WATER AS WORKING GASES

By Irene Sänger-Bredt

FOR REACTOR-HEATED ROCKET MOTORS

Translation of "Die Eigenschaften von Wasserstoff und Wasser als Arbeitsgase für kernenergetisch beheizte Raketentriebwerke."

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THE CHARACTERISTICS OF HYDROGEN
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FOR REACTOR-HEATED ROCKET MOTORS\*

By Irene Sänger-Bredt, \*\* DGRR

Abstract. In some fields of technical application—in particular with ballistic missiles of extremely long ranges—it would be desirable to employ a working medium, contained in a tank, with an energy higher by several orders of magnitude than has hitherto been available with steam boilers, and thereupon, to accelerate this working medium, possessing a very high enthalpy, by expansion in a Laval-type nozzle to the highest exhaust velocity possible. The technical difficulties inherent in this problem do not only consist of heating a suitable working medium to a sufficiently high enthalpy, but are even more to be found in controlling such high gas enthalpies with the tank walls exposed to the incandescent gas.

Under these aspects, hydrogen and water vapor have been investigated as to their applicability as working fluids.

Enthalpy-entropy diagrams have been computed for either gas, with complete regard to dissociation, as well as ionization, over the pressure range between 10<sup>+1</sup> and 10<sup>-5</sup> atm, and within the temperature range between 500 and 10,000°K. Therefrom, the exhaust velocities possible for water, or

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water vapor, have been derived and compared with one another, with suitable supplies of energy, and on the assumption of equilibrium ratios, at various pressure gradients in the nozzles. The influence of the specific heats of mixtures and the mean molecular weights, on the exhaust velocities attainable—before and after heating—have been shown in numerical examples for hydrogen, water, and helium. On the strength of the findings, additional hydrides of light elements have been examined as to their applicability as working fluids and among these, boron (III)-hydride, as well as methane, are recommended for more detailed computation.

In addition to the exhaust velocities, the heat transfers to the combustion chamber walls, occurring with equilibrium ratios, have been examined by way of comparisons of hydrogen, water, and helium, using parameters introduced earlier.

The influence exerted by non-equilibrium processes on heating and expansion has been discussed. First, three characteristic, hypothetical limiting cases of incomplete equilibrium setting are examined, comparatively. The kinetic energies obtainable in all three cases in the nozzle exit, with equal thermodynamic initial conditions in the combustion chamber, are comparatively computed with hydrogen and water. Thence, the probable extent and the form taken by divergencies from the energy equilibrium, that must actually be taken into account, when a working fluid is heated by means of an external energy source, have been considered.

In particular, three methods of heating a working fluid have been investigated, namely fission reactors, arcs and fusion reactors. Thereby the possibility arises that, when low-grade energy working fluids are blended with high-grade energy elementary particles, a special type of divergence from equilibrium may be important—this type of divergence being characterized through an overpopulation of the degree of freedom of ionization within the combustion chamber. The enthalpy bound by this process is, during discharge, probably convertible into kinetic energy but to a very small degree. Terms have been developed, representing this "primar," ionization of the working fluid, and the accompanying loss of enthalpy, as functions of the ionization energy of this working fluid, of the mass ratio of working fluid particles and energy carrier particles, as well as of the numerical ratio of either type of particle—with known temperatures of the combustion chamber and kinetic energies of the projectile particles. The ranges of energy and

mixture, in which losses through primary ionization are important, have been indicated through the example of the heating-up of H<sub>2</sub> or H<sub>2</sub>O by means of bombardment with electrons or a-particles. By means of the basic rocket equation the number of energy carriers to be supplied to the working fluid per unit time has been computed for the above examples—this number guaranteeing a definite thrust, or a definite, required, exhaust velocity of the rocket.

#### I. The Concept of Working Gas and its Function in Rocket Motors

In certain practical fields of application, and particularly in those concerned with rockets designed for extremely long ranges, it would be advantageous to endow a chambered working medium with an energy higher by several orders of magnitude than any hitherto attainable with steam boilers, in order subsequently to accelerate this ultra-high-enthalpy medium to the highest possible exhaust velocity by expansion through a Laval nozzle. Practical executions of this scheme will be attended not only by the technical difficulties which arise in heating an appropriate working medium to sufficiently high enthalpy, but also by the more serious problem presented by the control of heat transfer from the combustion gas to the chamber firewall at this high enthalpy.

An earlier investigation [18] has shown that these difficulties impose an upper limit upon the magnitude of energy concentrations controllable in rocket applications, and that this limit probably occurs at some level beyond the 10<sup>4</sup> kcal/kg-order of magnitude attainable in classical combustion processes (the "atomic-shell" reactions), but several orders below those of the yields obtained in nuclear reactions.

In order to exploit the range of energy concentrations between those of the classical, medium-exhaust-velocity combustion rockets and those of the purely nuclear vehicles, which are currently uncontrollable in practice, it has been proposed that the incandescent gaseous plasma produced in nuclear fusion or in electric-arc heating, or the electron gas evolved in beta-disintegration processes, or some other feasible energy concentrate consisting of particles of inherently high mass-specific energy  $h_{\rm E}$  and negligibly

small mass  $m = n_E \cdot m_E$ —henceforth designated collectively as the "energy carrier"—be diluted in the rocket by admixture of a "mass carrier" having the large total mass  $M = n_A \cdot m_A$  coupled with a negligibly low energy content  $h_A$  to produce the chamber enthalpy

$$h_{O} = (m \cdot h_{E} + M \cdot h_{A})/(m + M) \simeq \frac{m}{m + M} \cdot h_{E}$$
 (1)

which lies just within the controllable limit. At a combined-mass ratio  $\mathbf{K} = \mathbf{n_E} \cdot \mathbf{m_E} / \mathbf{n_A} \cdot \mathbf{m_A}$  between energy carrier and mass carrier, the ratio  $h_{\mathbf{F}}/h_{\mathbf{0}}$  of undiluted enthalpy to chamber enthalpy becomes (K+1)/K. The chamber enthalpy  $h_0$  per unit mass of the incandescent gaseous mixture is the sum of the component enthalpies of the energy- and mass carriers:  $h_0 = (K \cdot h_{0(E)} + h_{0(A)}) / (K + 1)$ . In this relationship,  $h_{0(E)}$  denotes the energy carrier enthalpy per unit mass of the energy carrier and ho(A) the mass-carrier enthalpy per unit mass of the mass carrier after mixing. Neglecting the mass of the energy carrier, we may write K = 0 and  $h_0 = h_{0(A)}$ . The mass carrier is referred to as the "working gas." The term "thermal-atomic rocket" has entrenched itself in usage as applying to vehicles powered in the manner just described. A more appropriate and more generally applicable term might be "indirect-drive" rocket, since the essential difference between the purely chemically-fueled and purely nuclear-powered rockets on the one hand and those employing an injected gas which does not participate in the production of energy on the other consists in the fact that the energy-and mass carriers are no longer identical in the latter. Thus there no longer exists any fixed relationship between the nature of the working gas and the energy with which it may be supplied, since the ratio in which energy carrier and mass carrier are combined may be varied at will.

It will be obvious that the above reasoning is not limited in its application to rockets, but is equally valid for jet-propulsion systems in which the entire supply of energy- and mass carriers is not carried on board—e.g., for ramjets.

Since optimal operating conditions such as chamber pressure, temperature, etc. for indirectly-driven rockets will differ markedly—in consequence of the added opportunity for variation inherent in their design—from those

for rockets whose thermal capacities are functions of the fuel used and independent of state, studies of the thermodynamic behavior of various working gases and the optimal operating conditions under which they produce the highest possible exhaust velocity with a minimum transfer of heat will be a prerequisite to the development of any motor of this type. The paramount significance of exhaust velocity in determining the performance of a rocket in flight is assumed to be a familiar matter [11, 19].

For the purposes of these introductory studies, we shall make certain basic assumptions—simplifying and/or restrictive—which will probably be inadmissible or imperfectly valid for some applications yet to arise. They are as follows:

- 1. Postulating an indefinitely large source of energy embodied in a vanishingly small mass and immediate, continuous transfer of energy from this source to the working gas, we consider only "natural" working gases—i.e., homogeneous chemical compounds formed stoichiometrically from atoms of the various elements and their isotopes and stable under normal terrestrial conditions, and not mixtures of isotopes of atoms, subatomic particles, and photons such as might, for example, issue from a reactor;
- 2. We require, for the present, that only equilibrium states prevail in combustion chamber and expansion nozzle, and assume, in addition, homogeneous pressure- and temperature distribution in the combustion chamber and in any cross-section of the nozzle as an aspect of a uni-dimensional, isentropic exhaust flow which is not subject to energy losses by friction or radiation.

The first-named restriction signifies, in practical terms, that the mass of the energy carrier is neglected. One reason for this is that in consideration of the actual mixture of energy- and mass carriers, the number of possible combinations of energy carrier, mass carrier and mixture ratio—i.e., the number of different mixtures to be studied—would become exceedingly large; another consists in the fact that the temperature of such a mixture would be largely determined at any given pressure, thus restricting in advance the experimental manipulation of variables of state which would be undertaken with a view to determining optimal operating conditions. Furthermore, such comprehensive treatment would necessitate digressions into technical details, prominent among which would be the mechanism of energy

transfer from the energy source to the working gas. We shall not wish to commit ourselves with respect to these matters until the results of fundamental research provide more stable bases for such commitments.

For similar reasons, the following investigations will be concerned only with the case of homogeneous pressure and temperature distribution, which, due to its high heat-transfer rate, represents the most unfavorable conditions from a technical view; thus we avoid consideration of special techniques for artificial dynamic cooling at the outset, together with treatment of boundary-layer formation and the particular laws governing three-dimensional flow in the nozzle. On the other hand, the deviations from overall energy equilibrium—the nature and scale of which are likewise determined extensively by the energy-transfer mechanism and the construction design of the rocket—shall not be entirely disregarded. In a special chapter following the investigations for instantaneous establishment of equilibrium the direction in which relaxation of individual degrees of freedom asserts itself is tentatively determined by study of extreme hypothetical limiting cases.

Emphasis must be placed upon the fact that not only the assumption of homogeneous pressure and temperature distribution specifies a most unfavorable case - for the reasons given above - but that also our neglect of the mass of the injected energy-carrier particles with their extremely low gram-molecular weights will at least reduce the total kinetic energy recovered at the end of the exhaust nozzle.

### II. Heating of Hydrogen and Water at Equ librium and Constant Pressure; Exit Velocities Attainable in the Expansion Nozzle

Of the substances which appear technically interesting as working gases, we select hydrogen and water for more detailed study.

These two substances were studied in the pressure range between 10<sup>+1</sup> and 10<sup>-5</sup> atmospheres and at temperatures ranging up to 10,000°K, assuming ideal-gas behavior. The components H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, O<sub>2</sub>, H<sub>2</sub>, OH, O, H, O<sup>+</sup>, H<sup>+</sup>, and e<sup>-</sup> were taken into account in computing concentrations in the working gas during its dissociation and ionization. A rough estimate indicated that the O<sup>-</sup> concentration could be neglected. The concentrations of the ionized

molecules  $O_2^+$ ,  $O_2^-$ ,  $H_2^+$ , and  $OH^+$  were also omitted from consideration, since ionization is detectible <u>before</u> completion of dissociation only at pressures above  $10^{+1}$  atmospheres. Further particulars concerning the computations—e.g., the partition functions employed and other thermochemical data—are the subject of a projected separate paper [21].

Fig. 1 shows as a result of these calculations curves for the degrees of dissociation and ionization of hydrogen and water vapor as functions of temperature and pressure. The degrees of dissociation and ionization of different working gases at the same temperature and pressure depend, of course, on the number, character, and atomic balance of the components in question, on the equilibrium cycles in which they may participate, and on their molar free enthalpies. In this presentation, the degree of dissociation or ionization is equivalent to the ratio of the sum of the partial pressures of all dissociation-or ionization products to the total prevailing pressure—i.e.,

$$D_{H_2} = (p_H + p_{H+})/(p - p_{e-}) = \frac{1 - n_{H+} - n_{H_2}}{1 - n_{H+}}$$
 (2)

or

$$D_{H_{2}O} = (p_{H_{2}} + p_{H} + p_{H+} + p_{OH} + p_{O_{2}} + p_{O} + p_{O+} + p_{O_{3}} + p_{H_{2}O_{2}})/(p - p_{e-})$$

$$= (1 - n_{H+} - n_{O+} - n_{H_{2}O})/(1 - n_{H+} - n_{O+})$$
(3)

and (after complete dissociation),

$$J_{H_2} = (p_{H^+} + p_{e^-})/p = 1 - n_H$$
 or 
$$J_{H_2O} = (p_{H^+} + p_{O^+} + p_{e^-})/p = 1 - n_H - n_O$$
 (4)

According to this definition, the degree of dissociation of H<sub>2</sub>O at the onset of dissociation as shown in Fig. 1 is several times as high as that of H<sub>2</sub> and when the variables of state are identical for both gases, since the dissociation of H<sub>2</sub>O into H<sub>2</sub> and O<sub>2</sub> begins earlier—i.e., at lower temperatures or higher pressures—than the decomposition of H<sub>2</sub> into H. This discrepancy diminishes gradually as the degrees of dissociation increase, since both values tend naturally to converge toward unity.

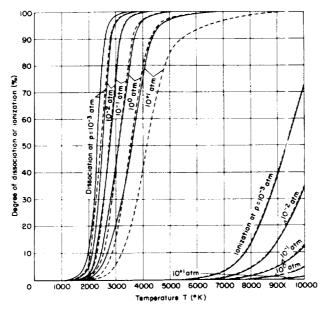


Fig. 1. Degrees of dissociation (ionization) in the working media water (\_\_\_\_\_) and hydrogen (----) as functions of pressure and temperature, assuming ideal equilibrium.

The degree of ionization of  $H_2O$  is less than 1% lower than that of  $H_2$  throughout the range of states studied, since the 1:2 ratio of oxygen atoms present in water in addition to hydrogen is characterized by an only slightly higher ionization energy.

Fig. 2 represents values for the average molecular weights of the two working media in question as functions of pressure and temperature, as obtained on the basis of the calculated component concentrations. In addition to absolute values of the molecular weights, the figure includes curves representing the square root of the ratio of the mass of water vapor to that of hydrogen as related to temperature and pressure. This quantity is an important factor to be considered in predicting the exhaust velocities attainable in rockets using these working media. In cases in which either of these working gases is completely dissociated, this ratio  $\sqrt{M_{H_2O}/M_{H_2}} = 2.441$ , and approaches its maximum, 2.989, at lower temperatures, attaining the latter figure when dissociation is completely suppressed. Due to the delay of

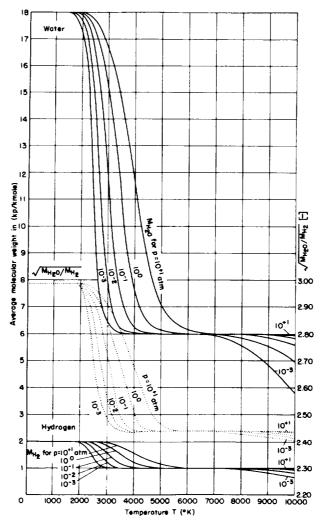


Fig. 2. Average molecular weights of the working gases water and hydrogen at equilibrium and the square root of the ratio of masses of these working gases, both presented as functions of temperature and pressure.

dissociation in  $H_2$  with respect to that of  $H_2O$ —a phenomenon discernible in Fig. 1—the ratio  $\sqrt{M_{H_2O}/M_{H_2}}$  may easily drop below the lower convergence value 2.441 for a short time in a range of states in which  $H_2O$  has just completed dissociation, remaining there until  $H_2$ -dissociation has also gone to completion. This scene is repeated once again in the range of the first

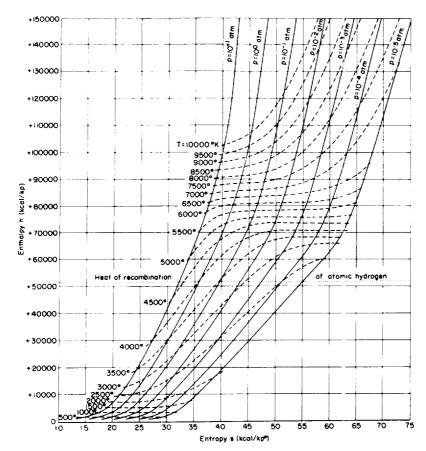


Fig. 3. Enthalpy-entropy diagram for hydrogen at equilibrium.

ionization stage, the convergence value remaining identical with that prevailing after completion of dissociation.

Figs. 3 and 4 are enthalpy-entropy diagrams containing isobars for pressures between  $10^{+1}$  and  $10^{-5}$  atmosphere and isotherms for temperatures between 500 and  $10,000^{\circ}$ K. The enthalpy-entropy diagram of Fig. 3, which was originally published several years ago [18] and is reproduced here only for purposes of comparison, applies to hydrogen; Fig. 4 gives the curves for water vapor. To give an indication of the upper limits of attainable exhaust velocity applying to direct-propulsion rockets in which hydrogen or water vapor serves as the mass carrier, the constant heating enthalpies which would be attainable in the rocket's chamber through a

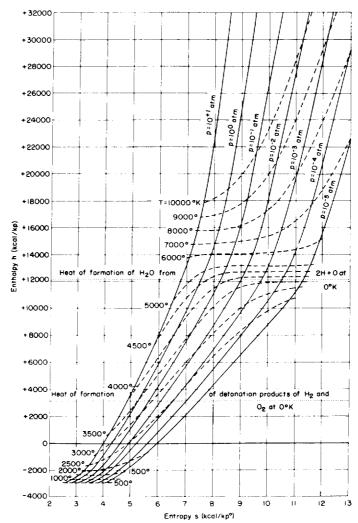


Fig. 4. Enthalpy-entropy diagram for water at equilibrium.

chemical reaction of maximal exothermal character leading to the formation of the mass carrier concerned are entered as dotted lines in the enthalpy-entropy diagrams. In the two cases under consideration here, these heat changes are those occurring in the recombination of monatomic hydrogen to form H<sub>2</sub> (51,210 kcal/kp) and in the formation of water vapor from H<sub>2</sub> and O<sub>2</sub> or from 2H and O (3,170 or 12,180 kcal/kp, respectively).

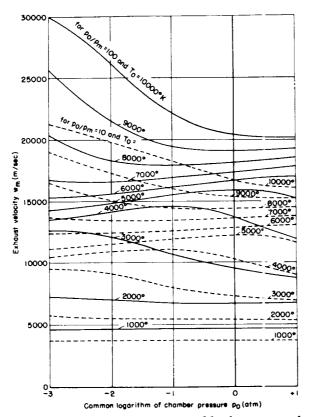


Fig. 5. Exhaust velocity  $w_m$  of hydrogen at the nozzle of a nuclear-chemically-powered rocket, presented as a function of chamber pressure  $p_0$ , chamber temperature  $T_0$ , and the expansion grandient  $p_0/p_m$  in the nozzle; immediate establishment of equilibrium is assumed.

The maximum exit velocities attained in the nozzle by this classical, fuel-conditioned chemical heating procedure show the usual uniform rate of increase as chamber pressure is elevated. For example, at  $p_0 = 10$  atmospheres and an expansion ratio of 100:1,

 $w_m = 14,265 \text{ m/sec}$  for hydrogen rockets, and  $w_m = 4,480 \text{ or } 6,650 \text{ m/sec}$  for water-vapor rockets of this type

In other words, the exhaust velocity of the hydrogen rocket is, in this case, about 3.2 to 2.1 times that of the other type, depending on whether a

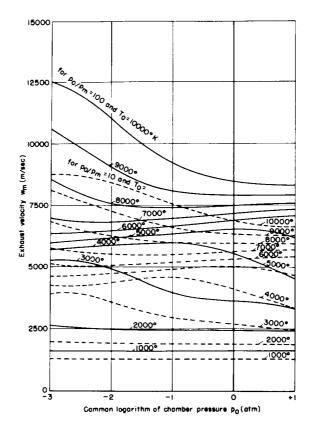


Fig. 6. Exhaust velocity  $w_{m}$  of water vapor at the nozzle of a nuclear-chemically-powered rocket, presented as a function of chamber pressure  $p_{0}$ , chamber temperature  $T_{0}$ , and the expansion gradient  $p_{0}/p_{m}$  in the nozzle; immediate establishment of equilibrium is assumed.

molecular or atomic stoichiometric hydrogen-oxygen mixture undergoes combustion to form the water vapor in the latter. It is also probable that the exhaust velocities attainable by complete recombination on monatomic hydrogen in a rocket are the highest to be achieved by any classical atomic-shell reaction. It must be noted in this connection that the instability of monatomic hydrogen has thus far prevented the materialization of any rocket design of this type. It is generally known that the exhaust velocities of liquid-fueled rockets in current use—e g., the V-2 and the Viking—lie between 2000 and 2500 m/sec.

Figs. 5 and 6 indicate, as functions of chamber pressure, the exhaust velocities theoretically attainable at various temperature levels in hydrogenand water-vapor rockets employing independent energy sources, assuming equilibrium conditions, isentropic exhaust flow, and expansion gradients  $p_0/p_m$  in the nozzle of 10 and 100. The shapes of the isotherms entered at thousand-degree intervals between 1000 and 10,000°K show local maxima and a general tendency to rise in the direction of lower chamber pressures. At a chamber pressure of  $10^{-3}$  atmosphere, an equilibrium temperature of 10,000°K and an expansion gradient of 100:1, the hydrogen rocket's exhaust velocity of 29,900 m/sec is 2.40 times that of the corresponding water-vapor rocket. An overall comparison of the two working gases on the basis of the dotted curve of Fig. 2 will show that the differences in attainable exhaust velocity—with the thermodynamic variables of state equal in both cases—are largely a reflection of the differing average molecular weights of the two gases under the conditions which originally prevail in the chamber.

Within our margins of mathematical error, the ratio of the exhaust velocities of these two working gases beyond about 4000°K remains practically equal to the square root of the reciprocal ratio of the corresponding molecular weights. At temperatures below 4000°K-i.e., in the range of steep dissociation gradients—the ratio of exhaust velocities wmH, /wmH,0 is characteristically somewhat smaller than the reciprocal ratio of the roots of the molecular weights; this discrepancy becomes more pronounced -at equal initial chamber pressures -as the nozzle-pressure gradient is amplified. In this temperature range, the superiority of hydrogen with respect to exhaust velocity is gradually reduced as the expansion gradient in the nozzle increases at constant chamber pressure, due to the earlier onset of dissociation in water. With a view to defining the influence exerted upon exhaust velocity by these secondary variables—namely, the molar specific heats of combination  $\sum\limits_{i} n_{i} H_{i}/T$  —more sharply than was possible by comparison of the highly similar dissociation and ionization curves of water vapor and hydrogen, the graph presented in Fig. 7 as an analog to Figs. 5 and 6 shows the exhaust velocities attainable using helium as a working gas with chamber pressures between 10-3 and 10+1 atmospheres and temperatures ranging from 1000 to 10,000°K. Since the degree of ionization of helium does not exceed 0.2% even in the least favorable corner of this range-

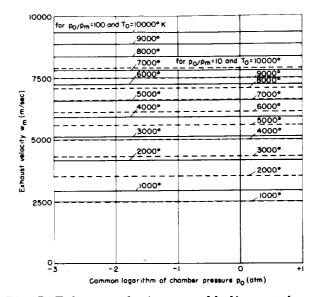


Fig. 7. Exhaust velocity  $w_{m}$  of helium at the nozzle of a nuclear-chemically-powered rocket, presented as a function of chamber pressure  $p_{0}$ , chamber temperature  $T_{0}$ , and the expansion gradient  $p_{0}/p_{m}$  in the nozzle; immediate establishment of equilibrium is assumed.

at 10,000°K and 10-3 atmospheres - it behaves as a purely monatomic gas with a constant molar specific heat of 5/2 · AR in the remainder of the range, and produces exhaust velocities independent of the absolute chamber pressure po. Comparison of the numerical exhaust-velocity values for helium (a velocity wm of only 9350 m/sec is attained with the chamber variables 10<sup>-3</sup> atmosphere and 10,000°K) with the corresponding figures for hydrogen (29,900 or 12,480 m/sec) shows that helium maintains exactly that position with respect to hydrogen and water vapor which its molecular weight dictates—namely, a position between hydrogen and water at low temperatures and a position beyond these substances at elevated temperatures—but that the actual exhaust-velocity figures are generally lower than the ratio of molecular weights would otherwise indicate. This is a consequence of the fact that given equal initial temperatures and pressures in the chamber, helium will, at this point, possess the lowest molar specific heat—i.e., the lowest potential enthalpy; moreover, only translational energy is liberated during expansion in the nozzle, since no contribution to the kinetic energy of the exhaust flow is made by molecular vibrational or rotational components

or released in recombinations from dissociated and ionized states.

We may nevertheless make the general statement that the ratio of their average molecular weights is the prime factor in determining the relative ability of working gases to produce high exhaust velocities in reaction-thrust motors; here, we refer not so much to the ratio in the normal, undissociated state of the medium which obtains prior to heating as to the ratio after dissociation or ionization is completed—or, in cases where the gases under comparative study dissociate or ionize in widely separated ranges of state, that of an intermediate condition. The molar enthalpy required for the attainment of a certain temperature level or a certain degree of decomposition is of only secondary importance as an indicator of possible exhaust velocity, and then on a much more modest scale.

### Working Gases, with Emphasis on Hydrogen Compounds of Light Elements.

The average molecular weights of certain compourds of light elements which may, under certain circumstances, be of interest as working gases are assembled in Table 1 for the purposes of the present discussion. To facilitate comparison, the absolute weight is followed in each instance by the value referred to that of hydrogen (in parentheses). Finally, the table contains the boiling points (\*K at 760 mm) of the substance listed, insofar as these values have been definitely established.

It will be evident that these figures possess genuine value for comparative purposes only in the event that the energy states denoted by the column headings occur in approximately the same thermodynamic range of states for all of the gases compared. These must also be attained at temperatures and pressures which fall within the limits of practical controllability. This last condition comes to the fore as the level of continuous recombination emission rises in areas of advanced ionization. The Supplementary Table 2 therefore presents a survey of the reaction heats [10] in kcal/kmole required to accomplish complete dissociation of the compared gases at the standard temperature of 25°C, as well as for the first and second ionizations of their component atoms, since it may be assumed as a coarse

TABLE 1

	Average molecular weight M								
Working Gas	Boiling point at 760 mm Hg (*K)	in undissociated state		after complete dissociation		after first ionization		after second ionization	
$H_2$	20.39	2.016	(1.000)	1.008	(1.000)	0.504	(1.000)	0.504	(1.000)
He	4,22	4.003	(1.986)	4.003	(3.971)	2.001	(3.971)	1.334	(2.647)
LiH	>953	7.948	(3.942)	3.974	(3.942)	1.987	(3.942)	1.590	(3.154)
BeH	?	10.021	(4.971)	5.011	(4.971)	2.505	(4.971)	2.004	(3.977)
$B_2H_6$	180.63	27.688	13.734)	3.461	(3.434)	1.731	(3,434)	1.538	(3.052)
CH <sub>4</sub>	111.67	16.042	(7.957)	3.208	(3.183)	1.604	(3,183)	1.458	(2.894)
NH <sub>3</sub>	239.73	17.032	(8.448)	4.258	(4.224)	2.129	(4.224)	1.892	(3.755)
H₂O	373,16	18.016	(8.936)	6.005	(5.958)	3 <b>.0</b> 03	(5.958)	2.574	(5.107)
HF	293.1	20.008	(9.925)	10.004	(9.925)	5.002	(9.925)	4.002	(7.940)

approximation that the temperatures at the start and completion of an endothermal decomposition process will increase with higher reaction enthalpies.

These values give a true indication of the order in which the completions of the individual decomposition processes occur along the ascending temperature scale only when certain restrictions are applied: namely, only in cases where decomposition does not occur in stages—as it usually does in dissociations of molecules consisting of more than two atoms—and where no different decomposition processes proceed concurrently, as in the ionization of the various dissociation products of a molecule. This disqualifies as directly comparable gases all those listed with the exceptions of hydrogen and helium; for the other substances, only an exact calculation could determine the extent to which the low average molecular weights of the dissociation—and ionization products in the rocket could actually be utilized to sustain exhaust velocity, and the thermodynamic range of states in which they would be effective.

Values in kcal/kp (decomposition product) for the global heats of reaction from the normal state to the degree of decomposition specified for any process may be derived from Tables 1 and 2 independently of the temperature and pressure at which the process in question reaches completion.

TABLE 2

Reaction	Heat of reaction E <sub>0</sub> (kcal/kmole)	Reaction	Heat of reaction E <sub>0</sub> (kcal/kmole)	Reaction	Heat of reaction E <sub>0</sub> (kcal/kmole)
H <sub>2</sub> → 2H	104 178	н → н+	314 999	_	_
_		He - He	568 340	He → He <sup>++</sup>	1 824 440
LiH <sub>Gas</sub> → Li <sub>Gas</sub> +H	58 459	Li → Li <sup>+</sup>	125 790	Li → Li <sup>++</sup>	1 871 130
$BeH_{Gas} \rightarrow Be_{Gas} + H$	50 619	Be → Be <sup>†</sup>	216 419	Be → Be <sup>++</sup>	637 763
$B_2H_6 \rightarrow 2B_{Gas} + 6H$	358 167	$B \rightarrow B^{+}$	192 800	B → B <sup>++</sup>	774 260
$CH_4 \rightarrow C_{Gas} + 4H$	397 943	$C \rightarrow C^{+}$	259 950	c - c++	823 583
$NH_3 \rightarrow N + 3H$	252 872	$N \rightarrow N^+$	336 913	$N \rightarrow N^{++}$	1 021 145
$H_2O \rightarrow O + 2H$	221 135	o <del></del> o <sup>+</sup>	315 500	0 - 0++	1 127 465
$HF \rightarrow F + H$	134 589	$F \rightarrow F^+$	403 250	F F <sup>++</sup>	1 211 380

TABLE 3

Work-	Global heats of reaction in kcal/kp and theoretical exhaust velocity in m/sec						
ing	after con dissociat	•	after compof first ionization		after completion of second ionization		
H <sub>2</sub>	$e_0 = 103 351$	w <sub>th</sub> = (29 400)	1 456 698	(110 000)	_	( - )	
He	_	( - )	283 957	(48 700)	1 367 646	(107 000)	
LiH	14 710	(11 100)	251 257	(45 800)	1 411 691	(108 700)	
BeH	10 102	(9 200)	232 350	(44 100)	500 689	(64 700)	
B <sub>2</sub> H <sub>6</sub>	103 487	(29 400)	1 521 526	(112 800)	2 468 583	(143 800)	
CH <sub>4</sub>	124 047	(32 200)	1 195 691	(100 000)	1 702 000	(119 400)	
NH <sub>3</sub>	59 387	(22 300)	720 893	(77 600)	1 172 840	(99 100)	
H <sub>2</sub> O	36 825	(17 500)	388 489	(57 000)	768 686	(80 200)	
HF	13 453	(10 600)	170 499	(37 800)	415 034	(58 900)	

From these values—neglecting, of course, the difference between the thermal enthalpies of the initial reacting substances and their products, and assuming complete transformation of the chemical potential energy of the dissociated or ionized working gas into kinetic energy—we may obtain, in turn, the so-called "theoretical" exhaust velocities w<sub>th</sub>. These reaction heats are assembled, together with the corresponding velocity figures, in Table 3.

All three tables confirm the indisputable superiority of hydrogen over all other working gases and in all thermodynamic ranges as regards attainable exhaust velocity. It is probable, in addition, that complete ionization is achieved earlier in hydrogen than in any other gas, and therefore that it reaches an emission-free condition at a relatively low temperature (aside from the nuclear emission which appears at temperatures beyond  $10^7 \, ^{\circ}$ K). This temperature may, for example, occur as low as 20,000°K at a gas pressure of  $10^{-3}$  atmospheres, and not exceed 50,000°K at 10 atmospheres. The figures given in the second and third columns of the tables for working gases having more than two electrons in their atomic shells are probably only of academic significance, due to the high level of recombination emission throughout the entire ionization range.

We may summarize as follows: desirable working gases will be compounds formed from the maximum possible number of atoms of light elements, having as large a hydrogen content as possible and the highest possible molar heat of decomposition. Assuming that the high heating enthalpy required for decomposition is available in unlimited and sufficiently "cheap" supply, gases such as these will produce the highest possible exhaust velocities in the rocket, since their exhaust-gas enthalpies per unit mass in the chamber  $(h_0)$  are maximal in consequence of their high molar enthalpy values and their low mean molecular weights in a state of dissociation, and their enthalpies at the nozzle opening  $(h_m)$ —at lower temperatures and correspondingly lower degrees of dissociation—are minimal in consequence of the great dissociation heats thus liberated and the concurrently increased molecular weights, with the result that the difference  $(h_0 - h_m)$  between these two enthalpies which is converted into the kinetic energy of the jet is correspondingly large.

Water, with an average molecular weight 9 to 5 times as great as that of hydrogen in all temperature ranges, assumes a relatively unfavorable position in the tabulation of potential working gases; this status will probably not

#### TABLE 4

a-Particle	a <b>= ½</b> He	$M_E = 4.00276$
β-Particle	$\beta \equiv e^- \text{ or } e^+$	$M_{\rm E} = 0.000 54_{\rm 9}$
Deuteron	$d = {}^{2}_{1}H$	$M_{\rm E} = 2.014 19$
Neutron	n <sub>≡</sub> dn	$M_{\rm E} = 1.008 98$
Proton	P≡ ¦H	$M_{\rm E} = 1.00759$
Triton	$t \equiv {}_1^3H$	$M_E = 3.02556$

admit of improvement, since water vapor is characterized by high levels of incandescent emission in all temperature ranges and an unmanageable degree of heat transfer to the chamber firewalls. Boron (III) hydride and methane, on the other hand, theoretically approach the performance of hydrogen in certain thermodynamic ranges of state, and it might therefore be profitable to undertake exact calculation of the enthalpy-entropy ciagrams of these two substances.

Finally, we should not overlook the fact that in certain energizing procedures involving direct bombardment of the cold working medium by highenergy subatomic particles, the average molecular weight  $M_F$  of the exhaust gas may be influenced, under the proper conditions, by admixture of such particles. The species, symbolic designations, and molecular weights of these particles are given in Table 4. With the exception of the neutron, the list contains only stable particles whose masses at rest differ from zero.

On the basis of the definition formula

$$M_F = \frac{n_E M_E + n_A M_A}{n_E + n_A}$$

and the relationship (1) pointed out at the beginning of this article, the relationship between the average molecular weight  $M_F$  of the exhaust gas—after mixing with the lighter particles having the molecular weight  $M_E$ —and the average molecular weight  $M_A$  of the working medium may be represented by the equation

$$M_{\rm F} = M_{\rm A} \cdot \frac{1}{1 + (M_{\rm A}/M_{\rm E} - 1)h_{\rm O}/h_{\rm E}}$$
 (5)

As this formula indicates, it is advantageous from the point of view of achieving the lowest possible value for M<sub>F</sub> to heat to the desired chamber enthalpy ho by means of bombardment with the greatest possible number of a particle species having minimal weight and an energy just slightly greater than ho. A rough numerical calculation will show that bombardment with neutrons, protons, deuterons, tritons, or alpha-particles from nuclear fusion reactions will hardly affect the average molecular weight of the working gas, due to the small number of particles n necessary per mole of working medium at the high energy ratio  $h_E/h_0$ . The bombardment of hydrogen gas with alphaparticles, for example, might, in theory, even lead to a slight increase in the average molecular weight after mixing. The bombardment of heavy working gases with relatively slow-moving electrons presents a totally different picture. With  $M_{\rm A}=10$ ,  $M_{\rm E}=5.5\cdot 10^{-4}$ , and  $h_0/h_{\rm E}=10^{-3}$ , for example,  $M_F \simeq M_A/19.2$ —a reduction of the average molecular weight to about a twentieth of its value prior to mixing and, judging from previous experience an indication of a more than fourfold increase in exhaust velocity.

#### Water, and Helium to the Firewall under Equilibrium Conditions.

As mentioned at the outset of this study, the difficulty encountered in development of thermal-atomic rockets lies not only in the attainment of the highest possible exhaust velocity at the nozzle, but principally in finding a means of controlling the accompanying transfer of large quantities of heat from the exhaust gas to the inner walls of the exhaust duct. We therefore proceed to an investigation of the heat-transfer phenomena which arise with the gases of our selected group under the same sets of thermodynamic conditions applied in previous discussions. It will be sufficient here, for purposes of comparison, to consider only the dynamics of the pressure chamber at negligibly low flow velocities. It will be remembered that any transfer of heat takes place via two routes, each of which is governed by its own peculiar set of laws and therefore requires separate treatment—namely, convection and radiation.

The derivation of the convection product as a measure of convective heat transfer has been discussed in an earlier article [18]. We repeat here only the essential conclusion that the so-called "convection product" ( $\gamma W h$ ) is that of the factors represented in the molecular enthalpy ( $\gamma h/N$ ) of the individual gas particle and the frequency ( $N \cdot \overline{W}$ ) of its collisions with the chamber wall, and therefore does in fact constitute a measure of the energy transported to the wall surface per unit time. Of the symbols used,  $\gamma$  denotes the specific gravity of the exhaust gas, h its enthalpy per kilogram,  $\overline{W}$  the average translation velocity of the gas molecules and N their number per unit volume. If the chamber contains a reacting mixture instead of a homogeneous gas, the convection product must accordingly first be calculated for each individual gas component and the sum

$$(\gamma \bar{\mathbf{w}} \mathbf{h}) = \sum_{i} (\gamma_{i} \bar{\mathbf{w}}_{i} \mathbf{h}_{i}) = \sqrt{8p^{2}/(\pi RT)} \cdot \sum_{i} \left[ \mathbf{n}_{i} \mathbf{H}_{i} / \sqrt{\mathbf{M}_{i}} \right]$$
 (6)

formed from the various partial transported energies; the product of the sums of partial values for  $\gamma$ ,  $\overline{w}$ , and hwould be incorrect.

The questions remaining open at this point are concerned with whether all particles which strike the wall also relinquish all of their thermal and chemical energy to it at once, whether they still retain their full chamber enthalpies in the vicinity of the wall in the first place, and, in the case of several recombination alternatives, with the types of percentages of particles which enter a specific recombination at the wall, liberating the chemical enthalpy characteristic of this recombination. If more information were available concerning the laws which govern this gas-kir etic mechanism, which might possibly yield to experimental studies employing molecular rays, we would not only be in a position to indicate exact values for convective transfers of heat, but might also be enabled, under certain circumstances, to control these transfers-for example, by employing anticatalytic agents to poison the chamber walls for highly exothermal recombination reactions, as has already been attempted in the case of recombination of monatomic hydrogen-here, by charging the chamber walls with gaseous  $H_2O$  or  $O_2$  or with syrupy phosphoric acid [7].

As in the calculation of exhaust velocities, it was assumed for the sake of simplification of the convection-product calculation (the result of which

does not pretend to be more than a parameter having purely comparative value) that the energy exchange between the gas particle and the surface of the wall is complete and instantaneous, and that the distribution of energy in the pressure chamber, including the marginal layers thereof, is perfectly homogeneous. The following model presentation was also applied: the firewall of the chamber is assumed to possess a characteristic enthalpy vanishingly small compared to that of the exhaust gas, with the result that every particle which collides with it will, under equilibrium conditions, immediately relinquish its entire thermal enthalpy to the wall. The colliding gas particle is further assumed to remain in the surface of the wall for a period of time sufficient to enable it to form—after colliding with a sufficient number of the other gas particles in the wall, to which the energy of the reaction is transmitted in each case—those compounds having the lowest relative chemical potential—i.e., H2 in the case of hydrogen, H2O in the case of water, H2O and CO2 in the case of oxygen-hydrocarbon mixtures, etc. Dissociations which occur upon bombardment of the wall by very high-speed particles and the accompanying loss of kinetic energy by the gas particles is neglected, so that our final selection of a basis for uniform comparison of all working gases is the least favorable—i.e., the highest—value for heat transfer to the wall.

These assumptions led to Fig. 8, which gives a logarithmic presentation of the convection products for hydrogen, helium, and water as functions of various exhaust-gas temperatures and pressures. To provide an indication of the significance to be attached to the numerical values implied by these curves, the Figure also contains the convection product of  $2.5 \cdot 10^7 \, \text{kcal/m}^2 \text{sec}$  as calculated for an ordinary oxygen-kerosene rocket and verified at the Trauen Experimental Station over 15 years ago—a value whose component convective and radiant heat transfers at 50 atmospheres combustion-gas pressure and 3550°K were even then effectively controlled at constant levels by means of forced-circulation water cooling. The convection products for hydrogen, water, and helium in the thermodynamic range under consideration—i.e., at pressures ranging up to 10 atmospheres and temperatures up to 10,000°K—all lie below this value.

For the rest, the most striking feature of Fig. 8 is the effect of absolute exhaust-gas pressure on the convection product. As a consequence of this linear pressure-dependency of the convection product, all working gases—given

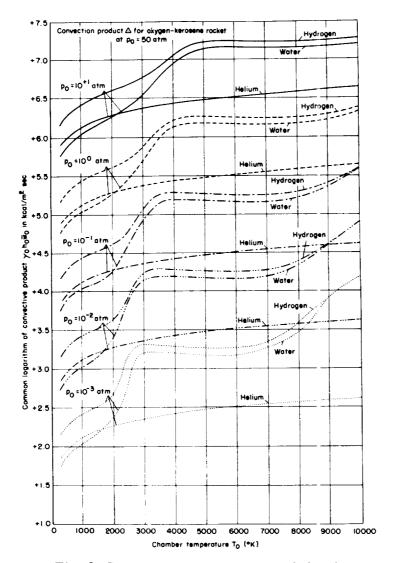


Fig. 8. Comparative presentation of chamber convective heat transfers for the working gases hydrogen, water, and helium as functions of temperature and pressure under equilibrium conditions.

equally large convective heat transfers—will permit increasingly higher exhaust velocities as the pressure declines, since the exhaust velocities themselves are either completely independent of pressure or, in the event of indirect relationship to pressure via the molar specific heats, even

increase on reduction of pressure. For the case of homogeneous, undissociated gases having constant specific heats, the maximum attainable exhaust velocities vary according to the following relationship, given equally large chamber convection products:

$$(w_m)_1/(w_m)_2 = \frac{(p_0)_2}{(p_0)_1} \sqrt{(c_p)_2 \left[1 - (p_m/p_0)^{AR/(c_p)_1}\right]} \sqrt{(c_p)_1 \left[1 - (p_m/p_0)^{AR/(c_p)_2}\right]}$$
 (7)

here,  $(C_p)_i$  are the molar specific heats of the two gases being compared and  $p_0/p_{\rm m}$  is the nozzle pressure gradient, which has the same value for both cases. Accordingly, at a constant rate of convective heat transfer to the chamber walls, such a working gas will produce higher exhaust velocities with each decline in its chamber pressure and its molar specific heat, irrespective of temperature and molecular weight. The assumption of constant specific heats made above is valid, with most gases, only at relatively high pressures and at such low temperatures that the absolute values attainable for exhaust velocity, even under optimum conditions, are uninteresting. The monatomic gases, which appear most attractive from this point of view, and for which the above assumptions are valid all the way up to the range in which ionization begins, permit exhaust velocities greater than 10,000 m/sec only at temperatures above 10,000 K where, for one thing, the corresponding convection products already exceed 107 kcal/m2sec and. for another, the assumptions of homogeneity of the gas and constant specific heats no longer have validity in the face of incipient ionization; moreover, the convective heat transfers are complemented by radiant transfers, which are proportional to functions of temperature rather than to the convection product. If different working gases are compared not on the basis of equal convection products, but at equal pressures and temperatures, it is readily seen that the exhaust velocities follow approximately the formula  $\sqrt{\sum_{i}n_{i}H_{i}}/\sqrt{\sum_{i}n_{i}M_{i}}$  while the convection products, on the other hand, vary as the expression  $\sum_{i=1}^{n_i} H_{ii} / \sqrt{M_i}$ ]. Thus both values increase with increasing specific heats and declining molecular weights, but at markedly different rates. It may be stated that in general the preference for one working gas over another is based not so much upon respect for a high exhaust velocity at equally high

convective heat transfers as on the mere assurance that a definite high exhaust velocity may be attained—with this gas and no other—in thermodynamic ranges which allow some relief from radiation; correspondingly higher convective heat transfers are accepted even though—under the assumptions which apply here—they can be tolerated only at the price of reductions in chamber pressure.

Specifically, Fig. 8 shows that in the low-temperature range below 2000°K, where only the small thermal components of the molar specific heats have begun to asset themselves, the convection products and exhaust velocities at equal temperatures and pressures increase in an almost linear sense with declining molecular weights (i.e., in the order  $H_2O$  - He -H2); here, therefore, according to the derivation given above for homogeneous gases with constant specific heats, helium delivers the relatively most attractive exhaust velocity, referred to equally large convective heat transfers, of all three gases under consideration, although its absolute value is not particularly impressive. At high temperatures, at which the molar specific heats of hydrogen and water increase in sharp contrast to those of helium as a reflection of the dissociation heats absorbed, the actual heat transfers from helium drop increasingly farther below those from hydrogen and water as the temperature is elevated. The exhaust velocities of helium, however, yield to those of water only at temperatures in excess of 7000°K, so that helium would appear to promise higher velocities than water, at lower heat transfers, in the range between 2000 and 7000°K. Throughout this range, hydrogen leads both gases by a wide margin with respect to both heat transfer and exhaust velocity. As temperatures increase and pressures decline still further - i.e., in the range in which ionization begins to manifest itself—the convection-product curves for water and hydrogen approach one another more closely, and finally follow practically coincident courses beyond the point at which the free-electron component

 $n_{e^-}\cdot H_{e^-}\sqrt{M_{e^-}}$  of the working gas, which, indeed, has consistently nearly identical values for both substances at equal temperatures, becomes the predominant factor in determining the convection product. This is the case at ionization degrees exceeding 35%. In these extreme ranges, therefore, hydrogen—at equal temperatures and pressures and even at equally large convective heat transfers—appears capable of delivering exhaust velocities superior to those of water by a large factor primarily determined by the ratio

of the average molecular weights. Helium may not be compared directly with the other two working gases in this respect, since it reaches the corresponding degree of ionization only at considerably higher temperatures or lower pressures than hydrogen and water. In the thermodynamic range under consideration, the convection product for helium at equal temperatures and pressures is smaller than those of the other two gases by one order of magnitude, and its exhaust velocity as much as two thirds lower.

An earlier investigation, which was concerned only with hydrogen, employed temperature as a comparative measure for heat transfers by radiation [18]. This parameter becomes inadequate when different working gases as well as different thermodynamic ranges are to be compared, since the coefficient by which the radiation level is related to a power of the temperature—and even this power itself—can no longer be regarded as constant. The specific radiation  $R = R_0(1-e^{-dn\sigma}) \approx R_0 dn\sigma$  will therefore serve as a measure for heat transfer by radiation in the present discussion. In this relationship,  $R_0$  is the specific radiation of a black body according to the Stefan-Boltzmann law, d is the thickness of the radiating layer (which, in this case, may be considered equal for practical purposes to the mean diameter of the chamber), n = p/kT refers to the number of gas particles per unit volume and  $\sigma$  to the mean effective optical cross-section. It was assumed in this theoretical treatment that the temperature of the irradiated wall surface is negligibly low.

Two fundamentally different types of radiation must be distinguished in calculating the specific radiations of working gases under equilibrium conditions:

- 1. The discontinuous emission of discrete wavelengths (lines or bands) characteristic of specific substances, which reflects the quantized nature of energy levels, and
- 2. The continuous recombination emission beyond the band edges which arises upon recombination of ions and electrons or of dissociated molecules with continuous velocity spectra.

The so-called resonance line emitted when an electron jumps from the lowest possible excited state to the ground state, or the characteristic temperature  $\theta_{el} = hc/(k\lambda) = 1.44 \cdot 10^{-8}/\lambda$  associated with this resonance line  $\lambda$ , is characteristic of the energy level of the working gas above which

For the energy levels at which recombination radiation is emitted, the prolecular heats of reaction  $\epsilon_0$  of these recombinations, or their characteristic temperatures  $\theta_{\rm ion} = \epsilon/k$ , are characteristic.

TABLE 5

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Element	Resonance line (ÅE)	Characteristic temperature for lowest excitation level (*K)	Characteristic temperature for first ionization (*K)	Temperature (°K) at 99.9% ionization at 10 <sup>-3</sup> atmosphere
н	1 215.68	118 100	158 500	15 100
He	584.4	245 700	280 006	24 400
Li	6 707.85	21 400	63 300	7 300
Ве	2 348.61	61 100	108 900	11 100
В	1 818.41	79 000	97 000	10 200
С	1 261.57	113 800	130 800	12 900
N	1 200.68	119 600	169 500	15 900
0	1 358.66	105 700	158 800	15 100
F	7 800.22	18 400	202 900	18 400

Numerical values for the resonance lines, characteristic electronic-excitation temperatures, and the correspondingly higher characteristic temperatures for simple ionization are assembled in Table 5 for a number of light elements. Since the characteristic temperatures may be regarded only as a convenient mathematical tool having temperature as their dimension, the actual temperatures at which the ionization process for the first shell electron is 99.9% complete at  $10^{-3}$  atmospheres are given in an additional column to provide more correct orientation. These were obtained by rough calculation with the Saha equation.

While the discontinuous radiations of a number of working gases may be negligibly small, their continuous recombination emissions acquire increased significance as the atoms become more heavily charged, although this occurs in a temperature range most of which lies above the 10,000°K limit which we have imposed.

By way of providing a numerical example, the specific radiation of hydrogen as a function of gas temperature is presented in Fig. 9 and waiculated for various chamber-gas pressures and a chamber diameter of our meter by a process developed by E. Sänger [15]. Included in the diagram

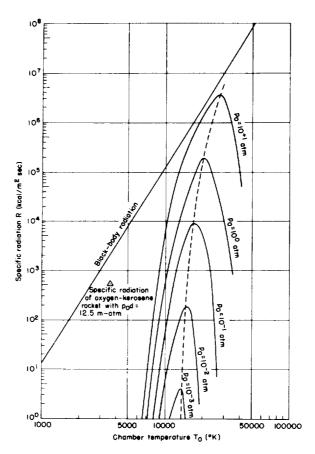


Fig. 9. Specific radiation of hydrogen gas at equilibrium as a function of temperature and pressure in the chamber at a chamber diameter d=100 cm.

as reference values are the possible maximum as given by black-body radiation and the specific radiation of the oxygen-kerosene rocket mentioned earlier as thermally quite controllable. It will be observed that radiation begins to assume critical proportions at about 9000°K and 1 atmosphere in a chamber of the diameter specified. However, at lower chamber pressures

which also permit better control of the convective transfer processes, the correspondingly larger chamber cross-sections may be satisfactorily controlled even at temperatures as high as 10,000°K.

Due to lack of data concerning the mean effective optical cross-sections of pure helium and water vapor, it is not yet possible to prepare analogous presentations for these two working gases. However, to judge from the values listed in Table 5, helium probably produces only negligible radiation in both the discontinuous and continuous ranges at the pressures specified here and temperatures below 10,000°K. Water vapor, on the other hand—as explained in greater detail in an earlier study by E. Sänger [12], should effect an appreciable heat-transfer volume even in the range of discontinuous emission. According to his figures, water radiates with an energy equal to 41% of that of the black body at temperatures as low as 2000°K with optically infinite layer thickness—i.e., at a rate of about 89 kcal/m² sec.

In consideration of its relatively low exhaust velocities coupled with high levels of total heat transfer, water vapor would therefore appear markedly inferior to hydrogen from a purely thermodynamic standpoint in which it is assumed that equilibrium prevails. Helium might possibly be of interest within a small range of temperatures just above 10,000°K, in which it begins to undergo ionization.

# V. The Influence of Non-Equilibrium Processes on Exhaust-Velocity and Heat-Transfer Values and on the Evaluation of the Various Working Gases.

The results of our investigations up to this point have all been obtained on the basis of the assumption of immediate and complete adjustment to equilibrium. It is, however, actually quite uncertain

- 1. whether the energy-transfer mechanism permits the working gas to achieve perfect equilibrium during its stay in the chamber;
- 2. whether, furthermore, the form of the nozzle permits immediate adjustment, in all of its cross sections, of all of the degrees of freedom of energy to the changing thermodynamic conditions during expansion; and finally

3. whether the fire gas molecules in the vicinity of the chamber wall still possess energies as high as those in the center of the chamber, and whether these energies are transferred completely to the wall by convection or radiation.

The following characteristics would be desirable from the viewpoint of the application for which the motor is intended:

- 1. due to the maximal exit velocities—referred to equal gas temperatures—which accompany it, energy equilibrium in the chamber [3], as well as
  - 2. subsequent isentropic expansion in the nozzle [2, 16], and
- 3. the sharpest possible energy gradient from the center of the flame to the firewall, coupled with maximum elasticity in the rebound of the gas molecule from the wall [13].

The foregoing calculations within the framework of the equilibrium assumption therefore present the most favorable case from the viewpoint of attainable exit velocities, but the least favorable with respect to convective heat transfers, if we conduct our comparison at the same chamber temperatures and if these temperatures are determined by the translational energy of the combustion gas. For comparison of attainable exhaust velocities at constant chamber enthalpy—as would be logical in the case of a direct chemical propulsion system, the requirement that full energy equilibrium prevail in the chamber and in the exhaust flow for the attainment of maximal exhaust velocity will by no means generally apply [3]. Nor would such a comparison be particularly interesting in the present study of indirect-propulsion systems, since these presuppose an energy source of virtually unlimited capacity, and the transfers of heat by radiation—which become significant, for the most part, only at high temperatures—are functions only of electron-excitation—and recombination temperatures and not of the total enthalpy.

Since the calculations based upon the assumption of complete transfer of energy at the boundary surfaces already yield the highest possible values for convective exchange of heat—i.e., represent the least favorable case, the quantitative effect of delay or suppression of energy exchange will not be derived here; instead, we merely enumerate the various known means by which the level of this heat transfer may be lowered at constant high chamber enthalpies. First, this may be done by artificially producing a

temperature gradient from the core of the chamber to the firewall by means of liquid [8] or gaseous [5] coolant films, by isolating the hot core of the plasma from the firewall, as might be accomplished with the aid of magnetic fields [1], etc., —or by any other means for artificial reduction of the enthalpy fraction which reaches the firewall under equilibrium conditions; another approach, however, involves elevation of the elastic reflection component of the gas molecules at the wall, either by the use of chemical coatings which produce an anticatalytic effect or by modifying the crystal structure of the wall surface, or even by charging the wall electrically. Among the measures listed above, the coolant films not only serve to lower the level of convective heat transfer, but offer a further advantage in their reduction of radiation to the wall. Finally, we mention the classical, and, in themselves, no longer adequate measures taken to cool the firewall, in which the heat already transferred from the gas to the wall is conducted through it to systems in which gaseous or liquid coolants circulate.

As concerns transfers of heat by radiation—processes which may, in principle, also be regarded as convective transfers by photons, in analogy to the convective heat transfers effected by particles having appreciable mass—it is impossible to make any explicit statement of the effect of non-equilibrium processes. On the one side, it is probable that at equal translation temperatures in the chamber, complete equilibrium adjustment in the working gas would deliver the lowest levels of heat transfer, since the pre-equilibrium period—as will be pointed out later—is almost invariably characterized by over-population of the degrees of freedom for electron excitation and excessive ionization. On the other side, the type of chemoluminescent emission which arises—in each case, on a no more than local scale—in confined spaces within the chamber is almost invariably absorbed to a large extent by the surrounding gas, and its intensity maximum displaced in the direction of longer wavelengths, before it reaches the solid firewalls of the chamber.

To provide a quantitative picture of the relationships between the degree of equilibrium adjustment and the attainable exhaust velocity in terms of specific examples, the chamber enthalpy  $h_0$  and the available kinetic energies  $w_m^2/2g$  as determined for hydrogen and water, respectively, by the different in gas enthalpies  $(h_0 - h_m)$  between the chamber and the nozzle opening that entered in Figs. 10 and 11 as functions of the chamber temperature due to

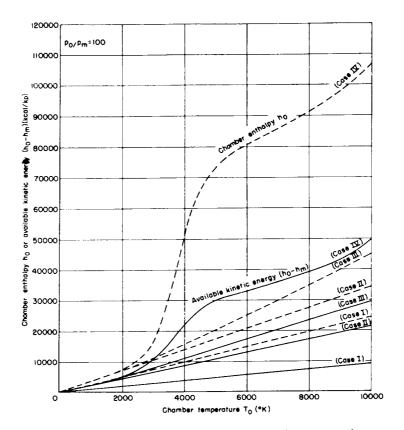


Fig. 10. Heating enthalpies  $h_0$  of hydrogen and the kinetic energies  $(h_0 - h_m)$  available therefrom by expansion from 1 atmosphere to 0.01 atmosphere in the nozzle, as functions of chamber temperature  $T_0$  and the degree of adjustment to equilibrium in the various degrees of freedom of energy during heating and expansion (Cases I through IV).

translational energy, for four hypothetical cases of equilibrium adaptation in which definite flow conditions are assumed—namely, a chamber pressure of one atmosphere and an expansion ratio of 100:1.

Of these, Case I represents the curve for immediate adjustment at equilibrium within the translational degrees of freedom in the chamber and the nozzle, and complete fixation of all other degrees of freedom in the condition in which they existed in the chamber before heating—e.g., at room temperature.

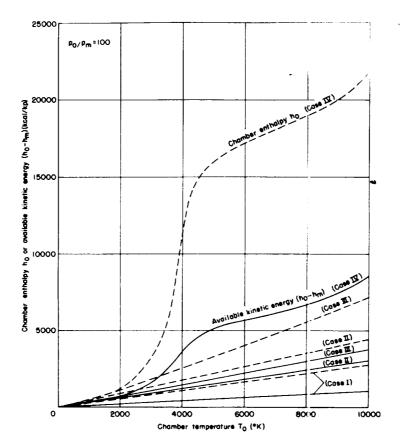


Fig. 11. Heating enthalpies  $h_0$  of water vapor and the kinetic energies  $(h_0 - h_m)$  available therefrom by expansion from 1 atmosphere to 0.01 atmosphere in the nozzle, as functions of chamber temperature  $T_0$  and the degree of adjustment to equilibrium in the various degrees of freedom of energy during heating and expansion (Cases I through IV).

Case II signifies immediate equilibrium adjustment in translation and rotation, and complete fixation of all other degrees of freedom.

Case III signifies immediate adjustment at equilibrium in the translational and in all internal degrees of freedom, and complete fixation of the captees of dissociation and ionization.

Finally, Case IV represents immediate equilibrium adjustment of all degrees of freedom, including the chemical reactions, in the chamber and the nozzle.

In Cases I through III, flow behavior is a function only of the temperature of the chamber and the pressure drop in the nozzle; in Case IV it is also affected by the absolute chamber pressure. In the calculation of the chemical enthalpy components for Case IV, the heat of formation of H<sub>2</sub> at 0°K was set equal to zero for the working gas hydrogen (Fig. 10); in considering water vapor (Fig. 11) the heat of formation of gaseous H<sub>2</sub>O was used as the corresponding base value.

As would be expected, the chamber enthalpy  $h_0$  at a given chamber temperature increases with the extent to which the various degrees of freedom of molecular energy are permitted to attain their saturation values for this temperature—i.e., with closer approximation of the ideal equilibrium condition achieved in moving from Case I to Case IV. The same applies for the enthalpy difference( $h_0 - h_m$ ), which increases on the one hand with the potential energy  $h_0$  of the chamber state and on the other with the extent to which the combustion gas in the nozzle adapts itself to the lowered temperatures and pressures by damping of all of its degrees of freedom and by release of thermochemical energy. Strictly speaking, the enthalpies and enthalpy differences of Case I, referred to unit mass, differ only in a sense determined by the inverse ratio of their molecular weights. As an effect of higher specific heats and the higher degree of dissociation of water, this difference decreases progressively—but, on the whole, only slightly—in Cases II, III, and IV.

If the degree of adjustment to equilibrium is not the same in the chamber and the nozzle, as it was in the four cases just discussed, but differs between these two areas—e.g., if in the chamber only translations and rotations responded immediately to excitation and all other degrees of freedom were fixed, while in the nozzle

- a) only the translational energies adapted immediately to the declining temperatures and pressures, with fixation of all other degrees of freedom in the states which prevailed in the chamber, or
- b) not only translations and rotations, but the molecular vibrations as well effected immediate equilibrium adjustment. Values lower than those of Case II would be obtained for the available kinetic energy  $(h_0 h_m)$  in either case. Specifically, the rotational component of the specific heats between  $T_0$  and  $T_m$  would remain unconverted into kinetic energy in Case IIa, while

in Case IIb the vibrational component of the specific heat between the low temperature prevailing prior to the warming-up of the chamber and the nozzle-exit temperature  $T_m$  would be lost as kinetic energy; exact calculation for these instances is further complicated by the fact that the exit temperature  $T_m$  at equal chamber temperatures  $T_0$  and pressure gradients  $p_0/p_m$  is different in all three cases, and highest in Case II, as a reflection of the different quasi- $\kappa$ -values which prevail during expansion [2, 16, 20].

In terms of this highly schematic treatment of the effect of delays in the adjustment to overall energy equilibrium or of the fixation of individual degrees of freedom upon the exhaust velocities attainable with a given gas at a given chamber temperature, let us now attempt to form an estimate of the extent and nature of deviations from energy equilibrium which must actually be reckoned with in the energization of a working medium. We may currently consider three fundamentally different techniques for heating such gases; these are distinguished in one respect by the temperature ranges in which they deliver the energy carrier.

1. In cases where an application of thermal energy between 102 and 103 °K is sufficient to heat the working medium, consideration is given to the use of fission reactors of types already proven in use [22]. Since in this event the necessary energy is supplied to the working gas by means of heat exchangers, the final temperature of the rocket champer will be strictly limited by the temperature tolerance of the solid reactor components and the mass of the energy carrier mixed with the working gas will be zero-i.e., the mass ratio between the energy carrier and the working medium in the chamber and in the expansion nozzle will become K = 0. Furthermore, full energy equilibrium will probably obtain in the chamber for this heating procedure—and, due to the low final temperatures and low flow velocities, quite possibly in the exhaust nozzle as well. There is no prospect of application of this method for high-performance engines, since the weight of the unit-including reactor, shielding, and pumping and injection systems becomes disproportionately great, while the exhaust velocities developed by the system remain so low that no advantage appears over and above those offered by direct-propulsion systems such as those of the thermochemical, liquid-fueled vehicles.

2. Where energy carriers with temperatures between approximately  $5 \cdot 10^3$  and  $5 \cdot 10^4$  K are adequate, a working medium may be heated by means of electric arcs. In this case, the energizing of the medium is not brought

about directly by nuclear energy, but through an electrical potential whic' may, of course, owe its existence to exploitation of nuclear energy, as would be the case if beta-decay batteries were employed after Kaeppler's proposal [6, 17].

The first working example of an indirect-propulsion rocket using water as its working gas and electric arcs as its energy sources was constructed on a laboratory scale by Peters [9] in 1954. In his experiments, a jet of water flowing as a spiral stream through a length of tubing formed a vortical canal a few millimeters in diameter; the axis of this canal contained the electric arc. The surrounding sheath of water is partially vaporized by the energy of the arc, and may be heated to plasma temperatures as high as 50,000°K in the axis of the discharge. The plasma, to which the vaporized water has imparted a pressure excess, flows through the anode-which is designed as a Laval nozzle—and into the environment with an exit velocity determined by the expansion ratio and the temperature of the arc. In this arrangement the water serves simultaneously as a stabilizer for the arc. as a cooling jacket, and as the working gas. The temperature gradient from the axis to the skirt of the arc is extraordinarily steep, being of the order of  $4 \cdot 10^4$  deg/mm. As a result of the gradual heating of the working medium from the liquid state, there is extensive energy equilibrium in the plasma within the chamber. To the best of the writer's knowledge, the significance of the part played by relaxation in the expansion nozzle has not yet been investigated. A further peculiarity of this experimental design is the fact that the electrical capacity of the arc, which first determines the temperature attained in a given vortical canal, determines the quantity of water vaporized per unit time and hence the plasma pressure built up in the chamber at the same stroke, so that of the three critical operating variables of the rocketchamber temperature, chamber pressure, and mass output—only one may be selected at will in each case. The Peters electric-arc rocket is certainly not the only possible solution to the problem of heating the working gas by means of electrical discharges. It is conceivable that the reciprocal effect between plasmas and their own or external magnetic fields might be exploited as a means of localizing the hot plasmas in the axis of the chamber, out of contact with the firewalls. Nor is it absolutely necessary that the arc canal and the heating chamber be identical entities. The gas chamber and the system which generates a corpuscular-ray beam might communicate, after Grün,

Schopper and Schumacher [4], via a series of "dynamic pressure stages" which permit corpuscular rays which have been produced, accelerated, and optically beamed in a vacuum to be channeled through free openings several millimeters in diameter into a gas chamber operating at atmospheric pressure. This method will permit any desired combination of working gas and electrically-charged energy carrier if the technical refinement of the pressure-stage system by the Heraeus organization is satisfactorily concluded—if this is not already the case. As alternatives to stationary electric arcs, flow discharges, cathode-ray tubes, electron guns, or the so-called "plasma pistols" [1] may be used as the corpuscular-ray generators in systems of this type.

A greater or lesser degree of deviation from overall energy equilibrium in the chamber is to be expected in applications of these procedures; in previous experience, this has usually asserted itself in overpopulation of electronic energy levels and ionizations. As a general rule, the departure of the chamber gas from equilibrium is the more pronounced as gas-kinetic collisions between the energy carrier and the working gas during their period in the chamber become less frequent, and as the discrepancy between their respective energies increases.

3. The chamber gas mixtures resulting from the application of fusion reactors operating on light-element nuclei as energy sources for the heating of working gases will probably be correspondingly far removed from equilibrium of energy. Here, the object would be to mix the products of nuclear-chemical fusion reactions, such as neutrons, a-particles, protons, high-speed electrons, etc., directly into the working gas in the chamber. Since the "temperatures" of the energy carriers in this still highly "futuristic" procedure are of the order of 10<sup>10</sup> K, the mixture ratio K in which energy carrier and working gas are combined might be very low indeed, if it may be assumed that the elementary particles actually expend their energy within the volume of the working gas. Under certain circumstances, this condition could lead to extremely large figures for minimum permissible chamber displacement, due to the low effective cross-sections of most working gases compared to those of violently accelerated subatomic particles, and those of neutrons in particular.

An additional technical difficulty to be expected will arise, according to Sänger [14], from the circumstance that the maintenance of a steady "flame"

with light-nucleus fusion reactions is possible only at such high chamber pressures and large chamber dimensions that the nuclear-fusion reactor itself may be conceived of only as a stationary, earthbound installation.

This superficial digression into the technology of the rocket with indirect propulsion system—the purpose of which was to shed light on the prospects for equilibrium adjustment in the jet gases of these motorsyields the conclusion that virtually total equilibrium may actually be achieved in the chamber and the nozzle with a number of heating techniques, but that the deviations from equilibrium which arise in the chamber upon application of other heating techniques take the form not only of underpopulation of certain degrees of freedom with respect to the levels attained in the ideal equilibrium condition—such as were considered alone in the schematized examples given in Figs. 10 and 11-but also of an initial overpopulation, especially of electronic energy levels and ionization; of these, the electron excitation decays rather rapidly to its final level, while the recombination which reverses primary ionization may be subject to appreciable delay. For this reason, the effect of this primary, pre-equilibrium ionization on the attainable exhaust-velocity values will be estimated on the basis of the extreme assumption that this ionization is not reversed in the chamber to any degree whatsoever. If we assume schematically that

1. Ionization of particles of species (A) is effected only by collisions with particles of any one species (i) whose relative velocity

$$v_r = \sqrt{v_A^2 + v_i^2 - 2v_A v_i \cos \varphi}$$
 (8)

together with their "reduced" mass

$$m_r = m_A \cdot m_i / (m_A + m_i)$$
 (9)

imparts to them a so-called "relative collision energy"  $m_r v_r^2/2$  greater than or equal to the required energy of ionization  $\epsilon_{ion}$ ;

- 2. further, that the frequency of reversal of such ionization processes is so low as to be negligible;
- 3. that stepwise ionization does not constitute a contribution to the primary ionization, but exerts its influence only in later stages of the adjustment to equilibrium, and

4. that no significant losses of energy by radiation or any other process occur, that the ratio dZ of ionizing collisions to the total number Z of all collisions occurring in a gas of uniform temperature T having equilibrium distribution in the translational degree of freedom will become

$$dZ/Z = \left(\frac{\epsilon_{1on}}{kT} + 1\right) \cdot e^{-\epsilon_{1on}/kT}$$
 (10)

This relationship may not be taken at face value in computation of the primary ionization of a working gas, since working gas and energy carrier possess widely divergent temperatures at the instant at which mixing occurs. Ionization begins in this pre-equilibrium state of the entire system, and is probably initiated by the bombardment of the "cold' working gas by foreign particles having either homogeneous high velocities  $v_{\rm E}$  or random translation velocities corresponding to an equilibrium temperature

$$T_{E} = \frac{2}{5} \frac{m_{E}}{k} \cdot h_{E}$$
 (11)

any of these particles which have kinetic energies between  $i \cdot \epsilon$  and  $(i+1)\epsilon i$  is capable of effecting ionization.

In cases where Maxwell velocity distributions of this type apply to the energy carrier, the ratio of the number of particles having a kinetic energy equal to or greater than  $\epsilon$  to the total number of particles is

$$\int_{\epsilon}^{\infty} \frac{dn_{E}}{n_{E}} = \frac{2}{\sqrt{\pi}} \left[ \left( \frac{\epsilon}{kT_{E}} \right)^{1/2} e^{-\epsilon / kT_{E}} + \int_{x=\sqrt{\epsilon / kT_{E}}}^{\infty} e^{-x^{2}} dx \right]$$
(12)

If the system velocity v<sub>E</sub> or the most probable molecular velocity

$$c_{E} = \sqrt{2k \cdot T_{E}/m_{E}}$$
 (13)

corresponding to  $T_E$  is so high relative to the most probable velocity  $c_A$  of the unheated working medium that the latter may be neglected as a contribution to the relative collision velocity  $v_r$ ,

$$n_{E}^{*} = n_{E} \cdot \frac{2}{\sqrt{\pi}} \sum_{i=1}^{n} \left[ \left( \frac{i\epsilon}{kT_{E}} \right)^{1/2} \cdot e^{-i\epsilon/kT_{E}} + \int_{x=\sqrt{i\epsilon/kT_{E}}}^{\infty} e^{-x^{2}} dx \right] = n_{E} \cdot f\left( \frac{\epsilon}{kT} \right)$$
(14)

out of n<sub>E</sub> bombarding projectile particles will, in the case of Maxwell velocity distribution, each effect one ionization among the molecules of the working gas, assuming that the density, depth, and effective cross-section of the gas are sufficiently great so that all n<sub>E</sub> projectiles make the necessary number of encounters in this passage through it—i.e., transfer their kinetic energy in full to the gas. In relationships (12) and (14),

$$\epsilon = \epsilon_{ion}(m_E + m_A)/m_A \tag{15}$$

and <u>i</u> denotes successive integers between 1 and  $\infty$ . The numerical values for  $n_E*/n_E$  are plotted as percentages in Fig. 12, as functions of  $\epsilon/kT$ , together with a broken curve which represents

$$\int_{\epsilon}^{\infty} dn_{E} / n_{E}$$

Thus if the indidence of projectile particles upon  $n_A$  molecules of working gas is denoted by  $n_E$ , the total ionization energy consumed in the reciprocal permeation is

$$n_E^* \cdot \epsilon_{10n} = \frac{n_E \cdot m_A}{m_E + m_A} \cdot \epsilon \cdot f\left(\frac{\epsilon}{kT_E}\right)$$
 (16)

Of the total enthalpy n<sub>E</sub>m<sub>E</sub>h<sub>E</sub> supplied to the working gas, therefore, there remains only a quantity

$$h_{O(A)} = \frac{n_{E}m_{E}}{n_{A}m_{A}} \frac{(5/2)k(T_{E} - T_{O}) - \epsilon_{1on} \cdot n_{E}*/n_{E}}{m_{E}}$$

$$= K \cdot \left[h_{E} - h_{O(E)} - \frac{m_{A}/m_{E}}{m_{A} + m_{E}} \cdot \epsilon \cdot f(\frac{\epsilon}{kT_{E}})\right]$$
(17)

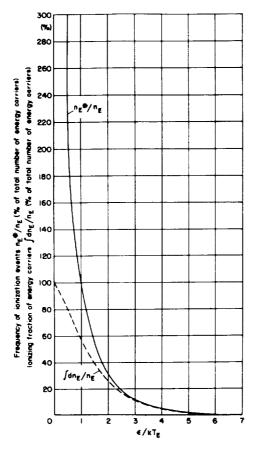


Fig. 12. Percentages of energy carriers effecting ionization and of ionization events possible in a working medium of sufficient density and depth, as related to the function  $\epsilon/k$   $T_E$ —at thermal equilibrium in the energy carrier—corresponding to a temperature  $T_E$  and a minimum kinetic energy  $\epsilon$  for ionization.

per unit volume of working gas to be used in heating the gas- and projectile particles to the chamber temperature  $T_0$ .

In the case of homogeneous velocity  $v_{\rm E}$  of the  $n_{\rm E}$  projectile particles, three alternatives are presented as regards the extent of the primary ionization:

1. if  $v_E < \sqrt{2\epsilon/m_E}$ , there is <u>no</u> primary ionization;

- 2. if  $\sqrt{2\epsilon/m_E} \le v_E < 2\sqrt{\epsilon/m_E}$ , each of the  $n_E$  particles effects one ionization in the working gas;
- 3. if  $v_E > 2\sqrt{\epsilon/m_E}$ , several successive working-gas particles may be ionized by each projectile particle, as is often actually the case.

In all three cases, Equation (17) takes the form

$$h_{O(A)} = K \left[ \frac{Av_E^2}{2} - h(E) - \frac{m_A/m_E}{m_A + m_E} \cdot i \cdot \epsilon \right]$$
 (18)

where <u>i</u> denotes the first whole number below  $v_E^2 m_E/2 \epsilon$ .

Since it is naturally impossible for the number of ionizations to exceed the total number of working-gas molecules present, Equation (17) applies only in the range  $f(\epsilon/(kT_E)) \leq n_A/n_E$ , and Equation (18) only in the range  $i \leq n_A/n_E$ .

At a certain given mass-specific energy

$$e_E = h_E + \frac{Av_E^2}{2}$$

of the energy carrier, and for a definite desired chamber enthalpy  $h_0$ , there will, consequently, be a maximal value for the mixed-mass ratio K, as given by the relationship

$$K_{\text{max}} = \frac{h_{O}(A) + \epsilon_{\text{ion}}/m_{A}}{e_{E} - h_{O}(E)}$$
(19)

this may in no case be exceeded.

If it is assumed as a limiting case of possible deviation from equilibrium, that primary ionization is not reversible—either during the concurrent thermal energization of the working gas in the chamber by lower-velocity collisions or during expansion of the heated gas in its passage through the nozzle—the results, although an additional part of the chamber enthalpy  $h_0$  will be required to achieve a given chamber temperature  $T_0$  and the convective transfer of heat will increase as a result of recombinations of ions at the firewalls, will not include a change in the kinetic energy available at the

nozzle exit at  $T_0$ , since only the absolute values and not the enthalpy difference  $(h_0 - h_m)$  will be affected. One technically interesting case would be that in which the primary energy of ionization is fixed in the chamber to the greatest possible degree, while the nozzle processes were influenced in such a way that extensive recombination occurred there, so that a more or less large fraction of the primary ionization energy became convertible into additional kinetic energy and exhaust velocities commensurately higher than those prevailing at the same gas temperature in the case of complete equilibrium.

For a given energy carrier and a given working gas, therefore, we may use the foregoing equations in calculation of numerical values for the primary ionization energy

$$e_{I} = \left[K\left(h_{E} - h_{O(E)}\right) - h_{O}\right]/(K + 1)$$

and the mass-mixture ratio  $K=n_{\mathbf{E}}m_{\mathbf{E}}/n_{\mathbf{A}}m_{\mathbf{A}}$  as functions of the chamber temperature as defined by the translational energy and of the translational temperature or system velocity of the energy carrier. The mass-mixture ratios and "fixated" primary ionizations are thus presented in Figs. 13 and 14 as functions of the residual chamber enthalpies for all possible combinations of hydrogen or water as the working gas with electrons or alphaparticles as energy carriers. This presentation incorporates the assumption that the energy carriers are subject to thermal velocity distributions corresponding to temperatures between 25,000 and 125,000°K, and that their energy level is retained in full, with uniform distribution, in the mixture of working gas and energy carrier. For the equilibrium situation in the chamber, two hypothetical limiting cases were considered: namely, those in which the estimated primary ionization energy according to Equation (16) is completely fixated and the residual energy of the energy carrier after subtraction of this component is transferred either in full to the translational degree of freedom of the mixture (translat onal equilibrium) or to all degrees of freedom of the mixture ("complete" equilibrium) with uniform distribution in each case corresponding to the equilibrium condition within the degrees of freedom considered.

The diagrams show that in temperature ranges in which the working gas at complete equilibrium is largely dissociated, the additional heat

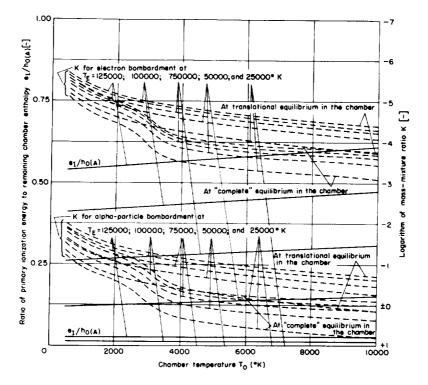


Fig. 13. Mass-mixture ratio K of energy carrier to working gas, and the ratio of expended ionization energy  $e_I$  to remaining chamber enthalpy  $h_0(A)$  as functions of chamber temperature  $T_0$  after mixing, for hydrogen as the working gas and bombardment with electrons or alpha-particles with thermal energy distribution corresponding to temperatures  $T_E$  between 25,000 and 125,000°K.

required to elevate all internal and chemical degrees of freedom to the translational temperature  $T_0$  necessitates a mixed-mass ratio of energy carrier to working gas about one order of magnitude greater than would otherwise be adequate. Any variation in the equilibrium adaptation of the chamber gas at constant chamber temperatures affects the level of the primary ionization energy in exact proportion to the corresponding chamber enthalpies, as expressed by the relationship

$$\frac{e_{I}}{h_{O(A)}} = \frac{(n_{E}^{*}/n_{E}) \cdot \epsilon_{ion}}{h_{E} - h_{O(E)} - (n_{E}^{*}/n_{E}) \cdot \epsilon_{ion}}$$
(20)

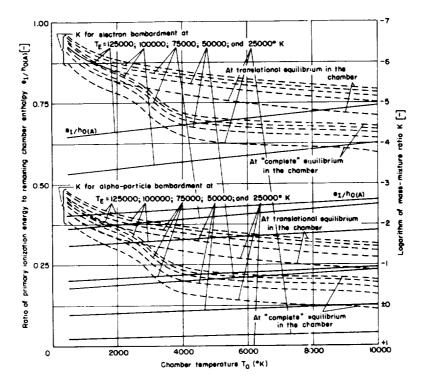


Fig. 14. Mass-mixture ratio K of energy carrier to working gas, and the ratio of expended ionization energy e<sub>I</sub> to the remaining chamber enthalpy h<sub>0</sub>(A), as functions of the chamber temperature T<sub>0</sub> after mixing, for water vapor as the working gas and bombardment with electrons or alphaparticles with thermal energy distribution corresponding to temperatures T<sub>E</sub> between 25,000 and 125,000°K.

Appreciable influence is exerted by the ratio  $m_{\text{A}}/m_{\text{E}}$  of the mass of the working-gas molecule to that of the energy carrier upon the values of the primary ionization energy and the mass-mixture ratio. The numerical values for  $T_{\text{E}} = 125,000^{\circ}\text{K}$  and  $T_0 = 10,000^{\circ}\text{K}$  are given in Table 6 for the cases treated in Figs. 13 and 14.

It will be seen at once that K increases sharply with increasing mass ratios, and e<sub>I</sub> with decreasing mass ratios.

Given the molecular-mass ratio  $m_{\mbox{\scriptsize A}}/m_{\mbox{\scriptsize E}}$  and the mass-mixture ratio K, the number of energy-carrier particles required per working-gas molecule may be computed by the formula

TABLE 6

Ratio of molecular masses of working gas and energy carrier	e <sub>I</sub> /h <sub>0</sub> (A)	K (for translational equilibrium)	K (for complete equilibrium)
$m_{H_2O}/m_{e^-} = 3.283 \cdot 10^4$	0.74	4.6 · 10-6	3.7 · 10 <sup>-5</sup>
$m_{H_2}/m_{e^-} = 3.674 \cdot 10^3$	0.61	3.8 · 10-5	1.7 · 10 <sup>-4</sup>
$m_{H_2O}/m_a = 4.501 \cdot 10^0$	0.45	2.8 · 10-2	2.2 • 10-1
$m_{H_2}/m_a = 5.037 \cdot 10^{-1}$	0.13	1.8 · 10 <sup>-1</sup>	$7.7 \cdot 10^{-1}$

$$\frac{n_{E}}{n_{A}} = K \cdot \frac{m_{A}}{m_{E}}$$
 (21)

Numerical evaluation—the results of which ranged between  $10^{+1}$  and  $10^{-2}$  in the examples under consideration—showed that  $n_E/n_A$  is predominantly a function of the ratio of enthalpies  $h_E/h_0$ , and much less so of the molecular mass ratio. A further indication was that the requirement that  $n_E* \leq n_A$ , which may become critical at high values of  $T_E$ ,  $T_0$ ,  $m_A/m_E$  and small values of  $\epsilon_{ion}$ —e.g., at  $T_E=125,000^\circ K$ ,  $T_0=10,000^\circ K$ , and electron-bombardment of water vapor—is satisfied over the entire range covered by the diagrams. In the low-temperature range—i.e., in bombardment of hydrogen gas by alpha-particles with temperatures up to and beyond 75,000°K or similar bombardment of water vapor with temperatures up to and exceeding 25,000°K, the energies supplied are no longer sufficient to produce any primary ionization whatever.

The number of energy-carrier particles to be injected into the working gas per unit time may be estimated, with the aid of the basic rocket equation  $P \cdot dt = w \cdot d (M+m)$ , as

$$dn_{E}/dt = \frac{K \cdot P}{(K+1)gm_{E}w}$$
 (22)

a relationship which gives figures between  $10^{22}$  and  $10^{27}$  per second for the cases under consideration, assuming a rocket producing a 10-ton thrust and

an exhaust velocity of 10,000 m/sec, or a constant mass output of 1 kg/sec. Plasma pistols capable of projecting  $10^{15}$  to  $10^{18}$  ions per pulse and operating with a pulse duration of  $10^{-7}$  sec would only approach the lower limit of this requirement, even assuming alternating, uninterrupted operation of more than one unit. Lower energy-carrier outputs would meet the requirements of this specified rocket only at higher energy-carrier temperatures and consequently lower values for K. The high-speed electron beam produced in Grün's experiments delivered only  $3 \cdot 10^{15}$  electrons per second, although these carried an energy of 50 keV corresponding to a uniform particle velocity  $v_E$  of  $1.3 \cdot 10^8$  m/sec or a particle temperature  $T_E = 2.3 \cdot 10^8$  K; ion beams generated in the same study possessed particle energies up to 600 keV, corresponding to  $v_E = 1.1 \cdot 10^7$  m/sec or  $T_E = 2.8 \cdot 10^9$  K.

Finally, if the  $n_{\rm E}/n_{\rm A}$  values are known, the average molecular weight of the jet gas may be calculated—taking the masses of the injected energy carriers into account, since, as implied in Section III, the differences between these and the average molecular weights of the pure working gases may well necessitate a correction of the exhaust velocities arrived at in Section II. The relationship

$$M_{F(k)} = (n_E/n_A \cdot M_E + M_{A(k)})/(n_E/n_A + 1)$$
 (23)

or

$$M_{F(k)}/M_{A(k)} = (K + 1)/(n_E/n_A + 1)$$
 (23a)

applies for the average molecular weight  $M_{F(k)}$  of the cold working gas or the energized working gas with fixed chemical equilibrium; this gives the following values for the mixtures listed in Table 6:

Water and electrons	$M_{F(k)}/M_{A(k)} = 0.868$ ,
Hydrogen and electrons	= 0.877,
Water and alpha-particles	= 0.913,
Hydrogen and alpha-partic	les = 1.08.

Similarly, for the average molecular weight M<sub>F</sub> of the heated gas with equi-

librium distribution of residual enthalpy over all degrees of freedom, we have the relationship

$$M_{\rm F} M_{\rm A} = \frac{(K+1)M_{\rm A}(k)/M_{\rm A}}{n_{\rm E}/n_{\rm A} + M_{\rm A}(k)/M_{\rm A}}$$
 (24)

This may be rendered equivalent to Equation (5), if we substitute K/(K+1) for  $h_0/h_E$  in (5)—an operation permissible only when primary ionization is negligibly slight. At a chamber temperature of  $10,000^{\circ}K$  and a chamber pressure of  $10^{-3}$  atmospheres, for example, the ratio  $M_{A(k)}/M_{A}$  for hydrogen would become 3.026, and that for water 4.678. These figures, used with the corresponding values for K in Equation (24), would yield for the same mixtures:

Water and electrons	$M_{\mathbf{F}}/M_{\mathbf{A}}$	= 0.795,
Hydrogen and electrons		= 0.832,
Water and alpha-particles		= 1.004,
Hydrogen and alpha-particl	es	= 1.566.

At lower temperatures  $T_E$  and correspondingly greater numbers of extremely light energy carriers, the ratio  $M_F/M_A$  may assume still lower values. Within the range represented in Figs. 13 and 14 they attain their minimum of 0.459 at  $T_E$  =25,000°K and  $T_0$ =10,000°K in the bombardment of water vapor with electrons.

The hypothetical limiting cases and quantitative examples discussed here can naturally give only an approximate picture of the problems which arise in consideration of the physical mechanism involved in the mixing of the working gas with the energy carrier and the finite periods of time for general adjustment of equilibrium after mixing, and which may, under certain circumstances, result in exchanges of "desirability ratings" among the working gases studied. Since it was consistently assumed for the purposes of the present discussion that the working-gas volume was sufficiently large to permit the energy carrier to dissipate its entire excess of energy within this volume, final judgments must be deferred until more exact studies of small chamber volumes have dealt with the effects of the effective

cross-section and decelerating capacity of the gas, with the specific ionization capacity of the projectile particles, etc.—all effects which depend not only on the natures of the working gas and energy carrier, but on their energy states as well. Finally, an investigation into the possibility of manipulating the recombination rate of primary ionizations might yield interesting results—e.g., indicate the extent to which the nature of the energy carrier affects this process, especially in cases involving electron bombardment.

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